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DEVELOPMENT OF HEAT-RESISTANT INTERLAYER

MATERIAL FOR LAMINATED GLASS

Johan Bjorksten
Luther L. Yaeger
Robert J. Roth

Bjorksten Research Laboratories, Inc.

December 1952

WRIGHT AIR DEVELOPMENT CENTER

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FOREWORD

ABSTRACT

Of the various materials investigated, Mylar (duPont poly ethylene glycol terephthalate) was the most effective heat resistant inter-layer for aircraft laminated glass. It withstands 400°F. for as long as two hours without apparent deleterious effects. Mylar-glass laminates maintain their shatter resistance throughout the temperature range of -65° to 400°F. and under differential pressures and temperature gradients simulating flight conditions.

Other polymers, which were not as satisfactory as Mylar because of insufficient thermal stability and/or poor optical properties, included:

> Cross-linked polyvinylbutyral
> Alcohol soluble polyamid (Nylon, type 8)
> Silicone elastomer
> Chlorofluoro polymer (Kel F)

Epoxy type adhesives produced the best bonding between Mylar and glass.

In view of the developmental nature of this work, these conclu-sions must be regarded as tentative and subject to further investigation. Further work on Mylar interlayers for glass laminates is being performed under Contract No. AF 33(600)-22723.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDING GENERAL:

M. E. Sorte
Colonel, USAF
Chief, Materials Laboratory
Directorate of Research

LIST OF ILLUSTRATIONS

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DEVELOPMENT OF HEAT-RESISTANT INTERLAYER MATERIAL

FOR LAMINATED GLASS

INTRODUCTION

Under Contract No. AF 33(038)-16240, an interlayer material was sought for aircraft laminated glass which maintained shatter resistance throughout the temperature range of -65°F. to 300°F. The following promising materials were evaluated in that work:

1. Cross-linked polyvinylbutyral
2. Alcohol soluble polyamide (Nylon, Type 8)
3. Silicones
4. Fluorinated resin (Kel F)
5. Polyurethanes
6. Unsaturated polyesters.

In the present investigation, the maintenance of shatter resistance was specified throughout the temperature range of -65°F. to 400°F. In addition, the interlayer material was to be capable of withstanding 400°F. for as long as two hours. The interlayer material was not restricted as to composition, bonding, or lamination procedure. However, the fluorinated resins and silicone resins were to be considered. The objective was a glass laminate that might be used in the transparent portions of supersonic aircraft. The glass must be able to withstand bullet penetration and not collapse when undergoing pressurized flight conditions, in addition to withstanding the temperatures encountered during supersonic flight and experienced when certain deicing systems are used.

Efforts were to be concentrated on the transparent interlayers from the fluorinated resins and from the siloxanes. Work on cross-linked polyvinylbutyral was to be essentially discontinued because the primary objective had been attained under the original contract. Work with the polyurethanes and unsaturated polyesters was suspended because of the relatively poor thermal stability, optical and/or fracture characteristics.

SECTION I

INTERLAYER MATERIALS

A number of interlayer materials were investigated. Earlier work with all of these materials, except Mylar (DuPont poly ethylene glycol tere-phthalate), had indicated their promise for glass laminates. As the superiority of Mylar for the target specifications became apparent, further investigation of these materials was discontinued in favor of work with Mylar. Nevertheless, because of the work performed with all of these materials under this contract, the following discussion of all the interlayers evaluated is presented here.

The interlayer materials which were investigated for glass laminates included:

        A. Cross-linked polyvinylbutyral
        B. Alcohol soluble polyamids (Nylon Type 8)
        C. Silicone elastomers
        D. Chlorofluoro polymer (Kel F)
        E. Mylar

These materials (A-D) proved less satisfactory than Mylar because of insufficient thermal stability or poor optical properties for the specified service conditions.

A. Cross-linked Polyvinylbutyral

From previous work with this material, a formulation of polyvinyl-butyral containing 35-40% of plasticizer and cross-linked with alkylurea-urea-formaldehyde resins or with acid catalysts was recommended. Reaction data on compositions which gave the best high and low temperature shatter resistance were evaluated to determine when the optimum molecular

weight increase had occurred. From these results, the effect of various

mixing procedures, curing cycles, and aging conditions could be evaluated.

The following milling and curing procedure was used for these

reactions:

a) Dissolve the additives in the plasticizer and distribute
uniformly through the butyral powder.

b) Warm for 3 hours at 50°C. (Use the maximum sized batch).

c) Mill on the Thropp mill with one roll at about 95°C. or lower
and with the water cooled opposite roll. When the mixture is
clear, stop the mill, record the time, insert a thermometer
in the center of the mass and record the temperature.

d) Remove the thermometer, start the mill, and separate the
rolls until the mass forms into a uniform slab around the hot
roll.

e) Stop the mill, slit the slab and peel off the milled polyvinyl-
butyral.

f) Cut the slab in half. Remill one half with the above roll
conditions. Check the mass temperature every 10 minutes
and remove samples of about a 10 gram size at the same time.

g) Stop milling after 1 hour (6 samples) if premature cross-
linking does not made the mass unworkable before this.

h) Dissolve the samples in anhydrous methanol to 7.5% concen-
tration. Examine for insoluble particles. If a clear solution
is obtained, measure and record the viscosity at a fixed
temperature. (i.e., 25°C.).

i) Take 6 samples from the other half of the slab which was not
reworked. Weigh these to get a 7.5% concentration for the
viscosity test as above.

j) Seal in individual jars but do not add methanol. Place jars
in 300°F. (150°C.) oven and remove after 0, 15, 30, 60, 120
and 240 minutes.

The viscosities were determined for 7.5% solutions of the resin in methanol with an Ostwald viscosimeter at a standard, constant temperature.

The results of this study are summarized in Table No. 1.

All of the compositions remained workable on the mill for over an hour but suffered pronounced decreases in viscosity as a result of this, indicating degradation of the polymer on prolonged milling. All compositions became cross-linked within 1/2 hour at 300°F.

The viscosity increase of L 703, after prolonged milling, indicates the start of cross-linking by the shorter, degraded polymer chains. This is undesirable at this point as the numerous cross-links formed by short chains will probably result in brittleness. For optimum low temperature toughness coupled with high temperature strength, the maximum length butyral chains coupled by occasional cross-links was sought.

REACTION DATA FOR CROSS-LINKED POLYVINYLBUTYRAL
(Butacite 62 parts, Flexol 3 GH 38 parts and indicated additives)

Sample No.	Additives	Milling time to become clear	Milling time after becoming clear	Efflux time (sec.)	Cure time 300°F. (min.)	Remarks
L 700	0.05 parts p-toluene sulfonic acid; 0.1 part Uformite MX61	14 min. at 79-82°C.	0 10 20 30 40 50 60	91.1 79.1 64.7 55.5 57.3 38.8 32.7	15 30 60	Efflux time 116.9 sec. Formed gelatinous mass Insoluble
L 703	1.0 part salicylic acid; 0.1 part Uformite MX61	50 min. at 73-83°C.	0 10 20 30 40 50 60	315.3 129.9 115.3 71.0 58.6 26.5 249.3	15 30 60	Formed gelatinous mass Insoluble Insoluble, slightly yellow
L 704	0.05 parts p-toluene sulfonic acid; 0.25 parts dimer acid	28 min. at 78-85°C.	10 20 30 40 50 60	150.7 142.4 136.4 110.5 117.9 109.8	15 30 60	Formed gelatinous mass Insoluble Insoluble, slightly yellow
L 705	0.05 parts p-toluene sulfonic acid; 1.0 part thymol	27 min. at 79-91°C.	0 10 20 30 40 50 60	121.0 291.3 243.5 245.3 237.8 235.1 229.5	15 30 60	Insoluble Insoluble, slightly yellow Insoluble, yellow

B. Alcohol-soluble Polyamids

Nylon films exhibited shortcomings as glass laminate interlayers at both elevated and lowered temperatures. At 400°F. they shriveled and darkened and at temperatures below 0°F. they were quite brittle. Benzyl alcohol as a plasticizer was effective in improving the low temperature properties of these interlayers but was subsequently abandoned as being too volatile.

C. Silicone Elastomers

Perhaps the outstanding characteristic of silicones is the comparatively slight effect of temperature on their strength or brittleness. Preliminary screening had indicated that commercially available silicones were not suitable for glass laminate interlayers because of their poor transparency, brittleness at low temperatures, and poor strength at elevated temperatures. However, it was believed that a transparent silicone could be produced and if its strength could be improved, this material would have great utility over a wide temperature range. Consequently, these materials were investigated further.

The patents and literature pertaining to silicone polymers with elastomeric properties were examined without disclosing any claims for transparent materials. Dow-Corning and the General Electric Companies were advised of the problem and asked for any assistance they might offer. Dow-Corning referred us to "Silastic 240", their unpigmented, translucent, elastomer. General Electric stated they were aware of the possible applications for the material but unfortunately had nothing to offer except the chlorosilane raw materials for elastomer synthesis.

As a starting point in work on silicone materials, the commercial elastomer and the monomeric building blocks (i.e., dimethyl dichlorosilane, methyl trichlorosilane, and dimethyl siloxane) for the proposed application were evaluated.

1. Silastic 240

The following tests and analyses were run to obtain basic information about the characteristics and properties of Silastic 240.

a) Light Transmission and Optical Density

Variation of Light Transmission with Thickness

Thickness of Uncured Gum (in thousandths of an inch)	Percent Light Transmitted (Based on densitometer readings)
10	88 (can see across room - cloudy)
20	78
30	73
50	58
115	30
265 (approximately 1/4 ")	11

By Coleman Spectrophotometer: from 300 to 800 mμ for a 16 mil film. 37% through 69% respectively (on uncured gum).

Wetting agents, or other additives, and hot and cold quenching of the films did not appreciably improve the light transmission as shown below:

    1 % sodium alkylsulfonate   - increased optical density.
    0.1 % sodium alkylsulfonate - no effect.
    0.1 % Sulfonate B   - no effect.
    0.1 % Sulfonex   - no effect.
    1.0 % Sulfonex   - increased optical density.
    0.1 % alkane sulfonic acid - no effect.
    1.0 % alkane sulfonic acid - increased optical density.

The variation of optical density with film thickness is nearly linear. When optical density is plotted against film thickness, a slope of 0.02 units of optical density per 0.003 inches thickness in the lower range and of 0.02 units per 0.004 inches thickness in the higher thickness range is observed (Laboratory determinations as per Wells, "The Present Status of Turbidity Measurements", Chemical Reviews, pp. 331-337, 1947).

As determined after different curing cycles at 125° and 150°, the optical density is independent of the curing cycle in this range, being slightly lower for films pressed at 125°C.

b) Chemical Analysis

In considering the possible structure of the material as $(R_2SiO)_x$, the following is the theoretical % ash for postulated R groups:

R Groups (2 of each)	Ratio: $\dfrac{SiO_2}{Monomer}$	% Ash-Theoretical
CH_3	60.1/74.1	81
C_2H_5	60.1/102	59
C_3H_7	60.1/130	46
C_4H_9	60.1/158	38
Phenyl	60.1/198	30
Et-O-	60.1/134	45
Bu-O-	60.1/194	32
$CH_2=CH=$	60.1/98	61
$CH_2=CH-CH_2-$	60.1/126	47

The percentage of ash actually determined was 44%. Consequently, Silastic 240 is not 90 or more mole % a dimethyl siloxane polymer. There would appear to be an appreciable quantity of the diphenyl siloxane polymer present.

Because the haze and opalescence of Silastic 240 might be attributed to the presence of silica, the material was analyzed for the presence of free silica. Samples were dissolved in concentrated sulfuric acid, centrifuged, and treated with hot diluted hydrochloric acid. There was no evidence of free silica.

The sodium fusion test was negative for the presence of halides.

c) Vacuum Destricutive Distillation of Silastic 240

For this purpose 150 grams of the resin and 20 grams of NaOH pellets were ground in a meat grinder 6 times and placed in a one liter, round bottom flask equipped with a Claisen head and manometer, and connected to a vacuum pump via two receivers cooled in a solid carbon dioxide-acetone misture. The resin was heated with the direct flame from a choked Meker burner for 12 hours. The pressure was maintained at 0-10 mm except under rapid gas evolution.

The following results were obtained:

Loss in weight	84.2 grams
Recovered volatiles	55.1 grams
Percent ash or residue	48.5 grams

Some crystals separated out. These melted at 60-61.5°C. on recrystallization. A yellow oil, approximately 48.5 grams, was the greatest fraction of volatiles. On fractionation, the following was separated:

Fractionation of Volatile Oil in Modified Engler 48.0 grams

Cut	Amount	Boiling Point °C.	n_D^{25}
1	2.5 ml	95-137	1.4067
2	5.3 grams crystals	134	----
3	10.0 ml	160-180	1.3923
4	3.5	137-181	1.4026
5	12.0	181-256	1.4175
Residue	9.0 ml yellow oil	> 256	1.4275

An aqueous extract of the oil gave a strong test for alde-
hydes and ketones. Positive tests for the benzenoid structure with
azoxybenzene-anhydrous $AlCl_3$ were obtained with the ash boiled
in water and extracted with petroleum ether, with cut #5, and with
the crude crystals obtained in the receivers.

Sodium fusion indicated the presence of sulfur.

2. Silanes and Siloxanes

In a pure form, dimethyl siloxane was hydrolyzed, condensed, and
cured with benzoyl peroxide. After condensation, the substance was clear
with slight coloration in a one inch thickness. As a 0.020" film, the materi-
al has a 95-100% light transmission. After being washed free of catalyst,
the material was slightly milky. Curing increased the coloration and de-
creased the light transmission to about 75%. The sodium fusion test indi-
cated a trace of halide.

Both dimethyl dichlorosilane and the dimethyl siloxane oil were
hydrolyzed and condensed. Difficulties were encountered with determination
of chlorine by volumetric methods due to variations in standard solutions and
discolorations due to suspected organic matter. Hydrolyses were effected by
simply adding the dichlorosilane to water kept at 10°C. The oil was sepa-
rated and dried over anhydrous sodium sulfate. The oil was then agitated
with small amounts of concentrated sulfuric acid for 15 minutes to 2 hours
at 100°-150°C. The gum was washed free of acid by mixing mechanically
with water or dissolving in petroleum ether and extracting with water. So-
lution in toluene and agitation in a Waring blender with water resulted in
emulsions stable to heat. Removal of the petroleum ether by evacuation
produced gelation at 25°C.

Dimethyl dichlorosilane was converted to a siloxane (preparation FFS-29) by reaction with mercuric oxide. A small yield of viscous oil was obtained. Benzoyl peroxide (3%) was incorporated in the siloxane gum (preparation FFS-30). Laminates were prepared by heating at 100°, 125°, 150°C. for 20 minutes and exhibited the following characteristics:

<u>100°C.</u> Very slight yellow tinge, slight adhesion, slight increase in tensile strength.

<u>125°C.</u> No change except slightly less adhesion.

<u>150°C.</u> No adhesion, slight increase in color (over 100), slight increase in strength.

As a preliminary test to standardize a cure procedure for the comparison of silicone gums as silicone rubbers, a batch was made up with TiO_2 pigment and benzoyl peroxide as follows:

A mixture of 30 grams of the prepared gum and 30 grams of pigment was milled with a 3% solution of benzoyl peroxide in 10 grams of redistilled toluene. The mass was milled cold and pressed for 12 hours at 200°C. between Kel F sheeting. A tough, elastic silicone rubber was formed with a tensile strength greater than 300 psi. A necessary improvement was a non-volatile solvent for the gum and peroxide which would not itself form peroxides. Dimethyl siloxane oil seemed the logical substance.

To prepare the chlorinated gum 5 grams of the dimethyl siloxane gum were spread out on a glass plate to a thickness of about 50 mils under a bell jar equipped with a 250 watt sun lamp generating 4% ultraviolet light. A U tube filled with carbon tetrachloride was adjusted to measure the static head on the .nixing flow of chlorine and nitrogen gases. The gaseous rates were adjusted to dilute the chlorine to a 1:10 mixture. The jar was filled with this mixture and irradiated for 16 hours. Preliminary runs with pure chlorine showed over-chlorination was indicated by brittleness of the resin and increased water solubility after treatment with 0.5 normal alkali. The gum was subsequently treated with molten potassium acetate which was then washed out and the gum dried. Samples of the final product were tested as follows:

1. Tesla coil (secondary 15,000 volts) with a film less than 100 mils
2. Oxalic acid at 150°C. for two hours
3. No. 3M RD Silon 602 (di-tertiary butoxy diamino silane)
4. Beta-propiolactone.

Improvement was slight to undetectable in all cases. With beta-propiolactone, discoloration was produced.

Mixing 0.5 grams of the slightly discolored gum with 50 mg. of laboratory atmospheric dust produced an optical density of 1.48 or 3-1/2% light transmission. Apparently dust has more effect on resins of refractive index of 1.41 than on the common plastics which have refractive indices of 1.50 and over.

For the evaluation of pressure treatments, 1.5 grams of the gum was dissolved in petroleum ether with 1 mole percent of ethyl silicate. The mixture was heated for five hours in an autoclave at 200-220°C. under an initial pressure of 300 psi in a nitrogen atmosphere. The final pressure was less than 1000 psi. The gum was transparent. The optical density of 0.09 was equivalent to 93.5% light transmission.

a) Purification of Silicone Raw Materials

For the synthesis of long chain, silicone elastomers with good clarity, extremely high purity of the dichlorosilanes and cyclic siloxanes is required. When present as impurities, trifunctional compounds cause premature cross-linking before the molecular weight can be built up to the desired degree, and monofunctional compounds terminate the chains with inactive groups which hinder further polymerization.

A series of distillation columns were designed and constructed to produce difunctional compounds of high purity. After testing to prove their efficiency, these columns produced the desired compounds to the established specifications.

The separation of chlorosilanes, as suggested by U. S. Patent 2,381,139, was also investigated. This process converts the chlorosilanes to 2-chloro-ethoxy derivatives by reaction with ethylene oxide. After fractionation of the derivatives, regeneration is accomplished with organic acid chloride and pyridine catalyst.

b) Condensation

The most satisfactory condensation procedure involved the heating of octamethyl tetrasiloxane with 1% of concentrated sulfuric acid at 150°C. for approximately 25 hours. Other satisfactory but somewhat less effective condensation agents included nitric acid, phosphorous pentoxide, and ferric sulfate.

c) Cross-Linking

Cross-linking by peroxides, ethoxy silanes, and agents which would cause ester, amide and various other linkages was investigated. Concentration on the action of peroxides revealed that benzoyl peroxide was the most efficient. The optimum procedure was to mix five percent by weight of peroxide intimately with the siloxane gum and to press the mixture between aluminum sheets for thirty minutes at 110°C.

Methyl triethoxy silane and tetraethoxy silane were used with slight success by dipping a cured film in them and heating in an oven for extended periods of time. When compounded directly into the gum they had an adverse effect on the curing action.

Cross-linking by other types of linkages was not as successful, because of the difficulty of chlorinating the methyl groups of the siloxanes.

d) Fillers

The strengthening effects of various fillers on siloxane films was examined.

When used in ratios of 1:1 and 1:2 by weight with siloxane, calcium fluoride and potassium chloride have a strengthening effect. However, they affect the transparency of the film adversely. Potassium cyanide has a strengthening effect on the film with very little effect on transparency.

e) Lamination

The use of a primer on the glass outerlayers was necessary to make the silicone resins adhere to glass. Although temperature has only a comparatively slight effect on strength and brittleness of this material, difficulty was experienced in avoiding the darkening of the interlayer at the laminating temperature of 175°C.

D. Chlorofluoro Polymer

For adhesion with Kel F, glass plates were treated before lamination with the reaction product of trichloro tertiary butanol and titanium tetrachloride. Adhesion was good, but the laminate properties were inferior to those with Mylar interlayers.

E. Mylar

Previous work with commercial, flexible polyesters as interlayers showed that they were unsuitable because of poor high temperature strength and brittleness when cold. Cross-linking by styrene or other monomers at the unsaturated position in their chains was also necessary to convert them from liquids to solid polymers.

Substitution of an aromatic, dicarboxylic acid for the aliphatic acid in the polyester resulted in higher softening points and marked changes in other physical properties. "Mylar" polyester (duPont poly ethylene glycol terephthalate) had many qualities required by the interlayer for glass laminates, as shown by the following data for 1 mil Mylar A:

Break tensile (psi)	25,000
Impact strength (kg.cm.)	105
Tear strength (gm)	29
Heat sealing temp. (°C.)	225

From "Properties of duPont Thin Films", 10/5/51, Film Dept., E. I. duPont de Nemours and Co., "Mylar" A is defined as a film with low fault count (a measure of pinholes or spots of dielectric weakness) for general use as an insulation and dielectric material. It can also be used in many non-electrical applications where a strong, durable material is required and freedom from static is not essential. Other recently introduced types are:

"Mylar" B - A film for general non-electrical uses, treated to decrease static.

"Mylar" C - A specially prepared high quality film with very low fault count and good high temperature insulation resistance, primarily for use as a dielectric in high temperature, high voltage capacitors.

"Mylar" D - A highly transparent film with a minimum of surface defects for plastic glazing and glass replacement applications.

In the next section are presented the data from tests for evaluating the different interlayer materials.

SECTION II

COMPARISON OF INTERLAYER MATERIALS

The interlayers which showed promise were incorporated into glass laminates with glass conforming to Specification AN-DD-G-551, Grade A, Type 1. Comparative data on the following properties of the most promising laminates were determined:

1. Haze and Light Transmittance
2. Shatterability (at significant temperatures throughout the specified range)
3. Stability under accelerated weathering (for Mylar laminates only as they were the only ones meeting the first two requirements.).

Additional information concerning lamination, curing, etc., has been reported when these factors were significantly different from standardized procedures.

A. Test Procedures

The properties indicated above were determined for promising laminates by the following techniques.

1. Haze and Light Transmittance

These characteristics of the prepared laminates were evaluated by Methods 3041 and 3021 of Federal Specifications L-P-406a with the apparatus in Figure 1. To determine the effects of elevated and/or lowered temperatures, the haze and light transmittance of the laminates were measured before and after exposure to these temperatures.
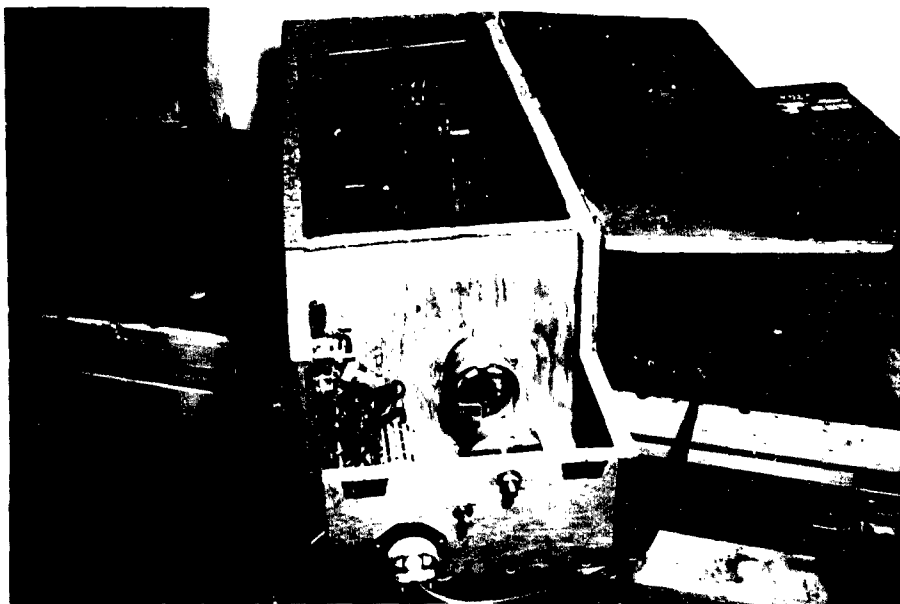
Figure 1. Apparatus for Measuremen.
of Haze and Light Transmittance.

2. Shatterability

In the initial testing of their shatterability, laminates exposed to specified temperatures (usually -30°F. and + 300°F.) were clamped in the Pressurized Testing Chamber (Figure 2). After the pressure differential had been established, these laminates were fractured by the impact of the falling hammer to which a simulated slug was affixed. In the data, the results of these tests are reported as the shatter resistance to low velocity slugs.

As the interlayers improved, this equipment was no longer satisfactory because the laminates resisted fracture by the hammer. For such laminates, the specified temperature extremes of -65° and 400°F., and the test chamber in Figure 3 were used. With this test chamber, power propelled H-91 type, .22 caliber steel projectiles (Figure 4) from the "Drive-It 300" power tool, distributed by Mounce and Cecil, Pittsburgh, Pa., were the means of fracturing the laminates. These results were reported as shatter resistance to high velocity slugs.

After fracture, the samples were rated for shatter-resistance, which was defined as the ability of the interlayer to retain the laminate as an integral structure. This property could be resolved into:

a. Glass adhesion to the interlayer after impact, and

b. Tear or shear resistance of the interlayer around the point of perforation.

3. Stability Under Accelerated Weathering

The laminates were exposed to accelerated weathering of 15 minutes under a carbon arc ultraviolet lamp and 3 minutes of rain in a Weatherometer for 200 hours.

Figure 2. Shatterability Testing Equipment.
The hot or cold laminate is clamped in the
window, air pressure applied, and the laminate
fractured by the steel slug at the end of the im-
pact hammer.

Figure 3. Pressurized Test Chamber. The heated or chilled laminate is clamped in the window, air pressure rapidly raised to the 6 psi in the chamber, and the laminate fractured by a steel projectile from the power tool shown at the left.
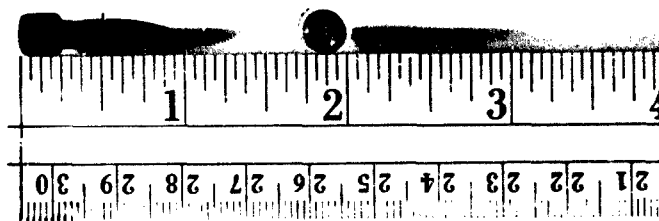
Figure 4. Side and End Views of H-91 type
Steel Pin used for Fracturing Glass Laminate.
The scale is in inches.

B. Results

Glass laminates were prepared with the various interlayers for evaluation by the above test procedures. Since the lamination techniques vary from interlayer to interlayer, the significant differences in laminating procedures are described below.

1. Lamination

a) Polyvinylbutyral and Nylon

Formed sheets were sandwiched between clean glass plates which were then wrapped in oil resistant, heat sealed bags of coated cellophane. The bags immersed under oil in the laminating autoclave were pressed at 200 psi, 275 – 300°F. for 1/2 hour.

b) Silicone Elastomers

The optimum cure for a 35 mil Silastic 240 film was its retention at 100°C. for 2 hours.

The glass plates were washed, dried, and cleaned with methyl alcohol. Uncured films were placed between the plates and held in a press with slight pressure until the above cycle was completed. The tensile strength of the resin was 460 to 500 psi at 90°C.

General Electric trifunctional SR-82 resin was ineffective when coated to 20 mils and lightly baked on as an adhesive.

c) Kel F

Glass plates treated with the reaction product of trichloro tertiary butanol and titanium tetrachloride were pressed against the fluorinated polymer film for 5 minutes at 265°C. The laminate was quickly transferred to another press at 120°C. and held under pressure until the interlayer had reached equilibrium at this temperature.

d) Mylar

Mylar-glass laminates resemble those with Kel F. Unlike polyvinylbutyral, which adheres directly to glass, a modification of the glass surface or inclusion of an adhesive phase was necessary. Pressing at 300-400 psi at temperatures near the softening point of the polymer effected an intimate bond but the optical quality was impaired. However, Mylar, unlike Kel F, does not appear to develop haze upon slow cooling.

2. Comparison of Interlayers

In the initial work before Mylar was used, the haze, transmittance, and shatter resistance of glass laminates with the other interlayers were determined. The properties of these laminates are shown in Table No. 2, and their shatter resistance at 300°F. and at -30°F., in Figures No. 5 and 6, respectively.

TABLE NO. 2

PROPERTIES OF GLASS LAMINATES WITH INDICATED INTERLAYERS

Sample No.	Interlayer	Thick-ness (mils)	Haze (%)	Trans. (%)	Shatter Resistance Under 6 psi air pressure	
					-30°F.	300°F.
Control	Butacite 3GH VC 100	30	3.0	97	Excellent	Adhesion good, Strength poor
Y-3	Butacite with 38% 3GH, cross-linked with 0.1% Uformite MX-61	30	2.5	90	Excellent	Good
TO-133	Nylon DV-55 with 0.1% salicylic acid and 30% benzyl alcohol plasticizer	8	1.5	91.8	Good	Adhesion good, Strength poor
TO-15	Nylon DV-55 with 0.1% salicylic acid (no plasticizer)	8	1.4	94.2	Adhesion good but brittle	Good
FF-17	Cured "Silastic 240"	35	>38	75	Good	Good
J-3311	"Trithene", Type A (Visking's extruded Kel F film)	6	2.9	91.5	Adhesion good but brittle	Good

TABLE NO. 2 (Contd.)

PROPERTIES OF GLASS LAMINATES WITH INDICATED INTERLAYERS

Nomenclature for Shatter Resistance:

Excellent — Impact hammer failed to perforate laminate. All glass particles adhere to interlayer and laminate retains its integral structure.

Good — Hammer point penetrates laminate. No other glass particles shatter from window. This type of fracture could be closed readily in an emergency.

Brittle — Laminate shatters like unlaminated glass.

Strength poor — Glass particles bent outward by escaping air. Large jagged opening formed.

About this time, Mylar laminates had been prepared and the properties of the laminates were determined at -65°F. and at 400°F. The shatter resistances of laminates with interlayers of cross-linked polyvinylbutyral, Mylar, and Silastic 240 are compared in Figure 7.

The thermal stability of these interlayers was determined by evaluating the effects on their light transmittance and haze after they had been exposed to 400°F. for 2 hours in a circulating air oven. After such exposure, cross-linked polyvinylbutyral bubbled severely and darkened at the edges. Nylon, Type 8, shriveled and darkened uniformly throughout. The initial optical properties, and after exposure to + 400°F., of Mylar, a transparent silicone elastomer, and Kel F are shown in Table No. 3.
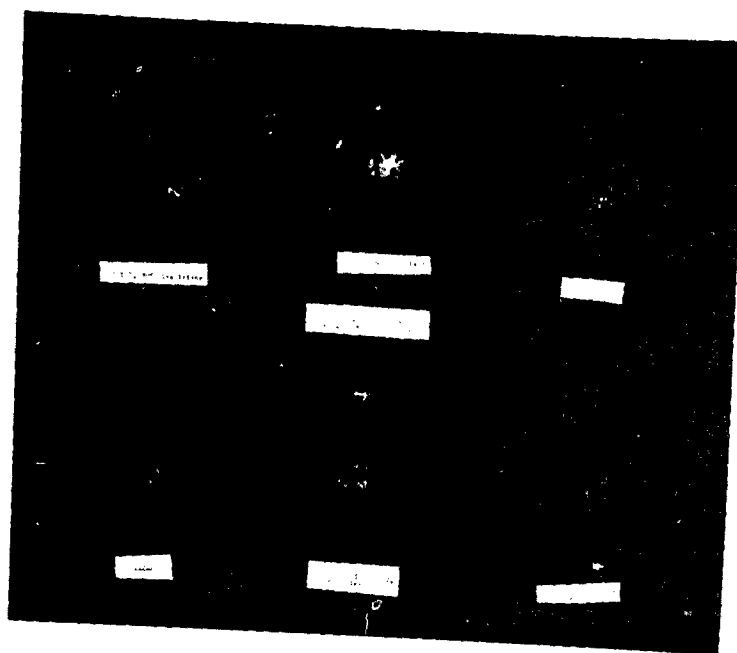
Figure 5. Laminates fractured at 300°F.
and a 6 psi air differential.
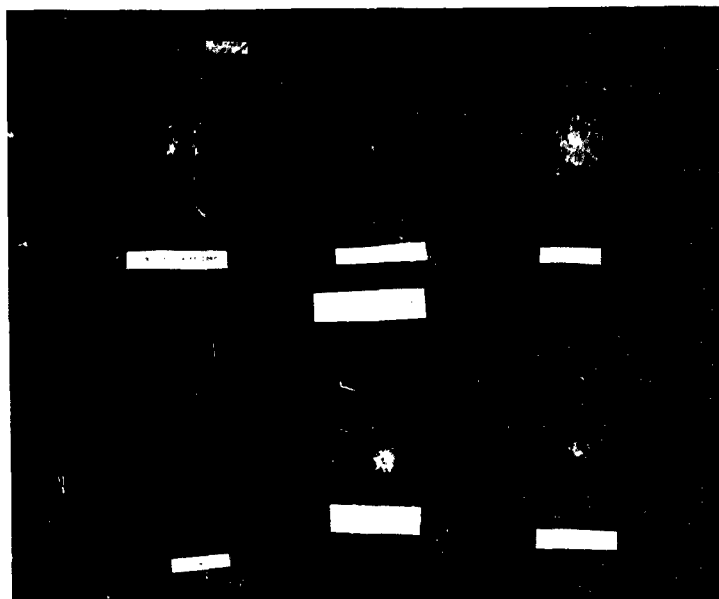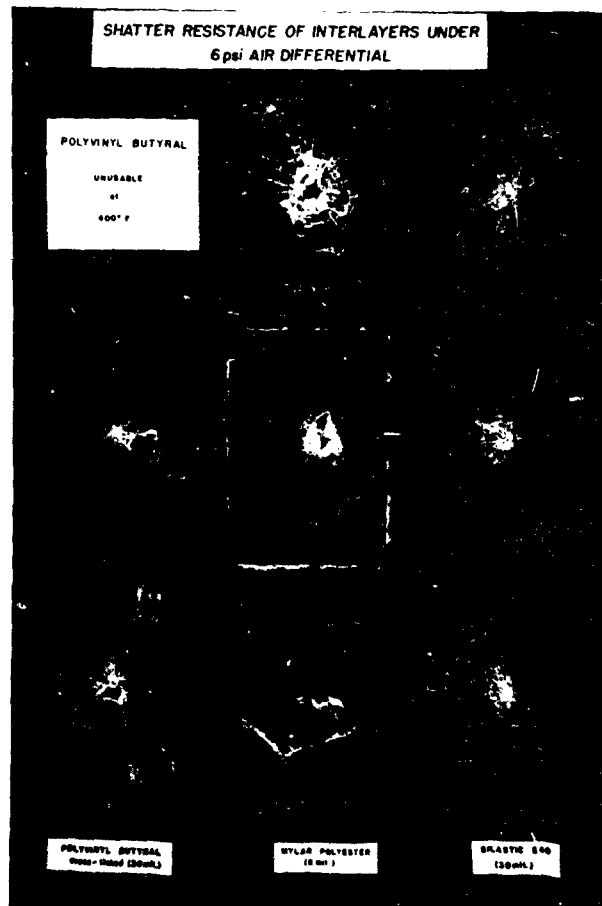
Figure 6.   Laminates fractured at -30°F.
and a 6 psi air differential.

Figure 7. Shatter Resistance of Laminates with
Interlayers of Cross-linked Polyvinylbutyral,
Mylar, and Silastic 240. (top row 400°F.,
middle row 300°F., bottom row -65°F.)

THERMAL STABILITY OF INTERLAYERS AFTER 2-HOUR EXPOSURE TO 400°F.

(As Shown By Light Transmittance and Haze)

Treatment	Mylar Polyester (2 mil)		Transparent Silicone Elastomer (13 mil)		Kel F (6 mil)	
	Trans.	Haze	Trans.	Haze	Trans.	Haze
Initial	92.2	1.5	85	17	91.5	2.1
After 2 hrs. at 400°F.	90.8	1.5	80	20	90.8	22.6

In the laminate form, the effect of the elevated temperature exposure on the interlayers is illustrated in Figure 8. The silicone elastomer in this work did not have the shatter resistance of the opalescent Silastic 240 which was previously discussed but was a clear polymer prepared by us from the condensation of octamethyl tetrasiloxane.

3. Conclusions

Although interlayers of the transparent silicone elastomer, Kel F, and Mylar did not decompose severely after a 2-hour exposure to 400°F., only Mylar retained sufficient clarity to be promising as a glazing interlayer after this test.

Adaptation of the silicone and fluorinated interlayers was considered beyond the scope of this project.

Consequently, emphasis was shifted to the preparation of Mylar-glass laminates. Mylar films as thin as 2 mils increased the shatter resistance of glass laminates at the elevated temperature but were brittle at -65°F. to slow velocity, high mass impact such as flak. When heavier film was used, the shatter resistance at -65°F. was improved.

HEAT STABILITY OF GLASS INTERLAYER
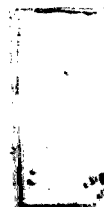AFTER 2 HOURS AT 400° F

TYPE 8 NYLON   CROSS-LINKED POLYVINYL
BUTYRAL
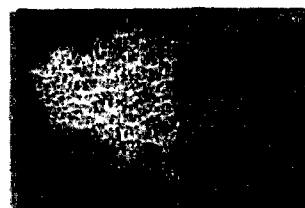
"MYLAR" POLYESTER   SILICONE ELASTOMER   "SEL-F"

Figure 8.   Comparison of Thermal Stability
of Glass Laminate Interlayers.

SECTION III

MYLAR-GLASS LAMINATES

Because of the demonstrated superiority of Mylar, especially after elevated temperature exposure, its use as an interlayer for glass laminates was investigated further.

Mylar films proved to be highly electrostatic so that difficulties were experienced in keeping the sheets free of dust or lint prior to lamination. A 3-inch "Static-master" (Nuclear Products Co., Costa Mesa, California) was effective in removing such contamination. This device consists of a fine camel's hair brush with a strip of shielded, radioactive polonium foil in the handle. The polonium precedes the brush bristles and ionizes the air above the sheet, temporarily dissipating the static charge and permitting the brush to remove the dust. To keep the interlayers and adhesive-coated glass free of dust until assembled, an enclosed working chamber was built with an attached air washing and filtering unit to supply ventilation (Figure 9).

Figure 9. Laminate Preparation Chamber.
Air entering the bottom of the large cone at
the right passes through a descending spray
of water, through the blower, and then through
a shredded aluminum foil before entering the
plastic film-enclosed working area.

In order to prepare Mylar-glass laminates with optimum properties, such factors as adhesives, curing agents, surface treatment of the laminate components, and lamination procedures were evaluated.

A. Adhesives

Two commercially available adhesives, EC 776 (Minnesota Mining and Manufacturing Co.) and PW 1-2 (St. Clair Rubber Co.), were recommended to us for use with Mylar. When laminates prepared with these adhesives were heated above 300°F., adhesion was impaired and the adhesives turned brown.

Epoxy type adhesives were more satisfactory for high temperature strength and color stability.

Araldite AN 111 (Ciba, Inc.) is a thermosetting polymer of this type which gave improved results. It is supplied in methylethyl ketone which evaporates from the glass plate to leave a clear, soft but dry, resin film. The dry resin melts as the laminating cycle begins and the excess flows from the edges when pressure is applied. As the temperature rises, the remaining adhesive gels and polymerizes to a transparent, glassy state. Some shrinkage of the adhesive occurs during gelation, causing voids in the laminate if sufficient pressure is not applied to compensate for this. A suitable cycle is the application of 200-300 psi at 325-340°F. for 1/2 hour. The cured Araldite adhesive phase, as well as the Mylar, withstands the 400°F. exposure test without discoloration or hazing.

In the thermoplastic state, Araldite does not wet glass well, so that a coating of the adhesive does not remain uniformly distributed on glass when heated to the softening point of the resin. Various cleaning agents such as acetone, household cleaner, and chromic acid do not improve the wetting properties of the glass.

However, surface treatment of the glass with organophilic agents greatly improved the wettability of the glass by Araldite AN 111. Methacrylatochromic chloride (duPont "Volan") a Werner type chromium complex, and vinyltrichlorosilane are both effective for this purpose. Vinyltrichlorosilane was preferred because of its better high temperature stability.

The presence of methylethyl ketone solvent in Araldite AN 111 adhesive complicates lamination, since the solvent must be removed before lamination. For this reason, liquid Epon resins (Shell Development Co.) were adopted as Mylar-to-glass adhesives. These resins are available in a wide range of viscosities.

Epon 562, a low viscosity resin of light amber color, was selected for adhesive application because of the ease of lamination. The low viscosity of this resin before curing results in a thin film of adhesive in the final laminate due to exudation of the adhesive in the press cycle. Blending Epon 562 with Epon 864, an extremely viscous resin of the consistency of pitch, permits wide viscosity control of the uncured adhesive and higher retention of adhesive in the press cycle. The optimal proportions were 15 parts of Epon 864 to 85 parts of 562.

B. Curing Agents

Amides, amines, dibasic acids, and acid anhydrides are useful curing agents for epoxy resins. Dicyandiamide, acids, and anhydrides are moderately soluble-to-insoluble in the resin and require ketones with or without water to effect solution of the curing agent in the resin. As noted previously, the presence of solvents complicates the laminating procedure.

Phthalic anhydride is soluble in Epon 562 to the extent of about 25 parts per hundred parts of resin when heated to 100°F. However, laminates made with phthalic anhydride-cured Epon 562 had localized areas of bond failure to the Mylar. This defect was associated with the Mylar, since the pattern of bond failure depended on the orientation of the Mylar in the laminate.

DMP-30 triacetate (tri(dimethylaminoethyl) phenol triacetate) (Shell Development Co.) is soluble in Epon resins without solubilizing additives. Except for the work with phthalic anhydride noted above, Epon resins were cured with this material.

C. Surface Treatment

The bond between the laminate components is improved by treating Mylar film with vinyltrichlorosilane. In shatter tests of laminates thus treated, the interlayer was sheared without serious delamination. There was no significant improvement in the bond strength by treating the glass with vinyltrichlorosilane.

Mylar is treated by immersing the film in 2% vinyltrichlorosilane in xylene for 10 seconds, air drying, and washing with water. Mylar is unaffected by xylene in this treatment.

D. Lamination

Mylar-glass laminates were prepared by using Epon adhesives without special equipment, as follows:

1) The adhesive resin containing the proper amount of curing agent is poured upon clean glass plates of the desired laminate dimensions.

2) Mylar film is positioned and rolled into contact with a steel hand roller to distribute the adhesive.

3) A second quantity of adhesive is then poured on one end of the Mylar, one end of the second glass plate contacted with the adhesive, and the glass lowered into place.

4) The flow of resin between the glass and Mylar as the glass is lowered sweeps air out of the laminate.

This method yielded laminates practically free of occluded air bubbles.

E. Properties of Mylar-glass Laminates

The haze and light transmittance, shatter resistance, and resistance to weathering of these laminates were evaluated by the previously described test procedures.

1. Haze and Light Transmittance

These characteristics of Mylar, both in the film form before lamination and in glass laminates, are reported in Table No. 4. Haze in Mylar increases with its thickness, the relatively high haze in thick film being an inherent property of the material. Consequently, the reduction of haze by modification of the film was considered beyond the scope of the work on this contract.

Occasionally, laminates using Epon adhesives developed a light amber color in local areas, which was probably the result of local over-heating.

TABLE NO. 4

HAZE AND LIGHT TRANSMITTANCE OF MYLAR
(As Film and Interlayer)

| | Film Thickness | | | | | |
| | .002" | | .007" | | 011" | |
	Haze	Trans.	Haze	Trans.	Haze	Trans.
Unlaminated	1.9%	93.5%	1.5%	95.5%	4.1%	95.5%
Laminated and cured	2.0%	93.2%	2.0%	94.5%	2.7%	91.5%
Laminated, cured, and heated 2 hrs.	2.8%	96.4%	2.0%	92.5%	4.4%	92.5%

2. Shatter Resistance

The shatter resistance of Mylar-glass laminates, 6" x 12" in size, when subjected to a differential pressure of 6 psi and the specified temperatures is shown in Table No. 5.

Figures 10-12 illustrate the shatter resistance of such laminates. At elevated temperatures, Epon resins cured with DMP-30, tend to become brittle (Figure 12, laminate at upper right). Under all the other conditions, the laminates, especially with 0.007" Mylar interlayers, exhibited superior shatter resistance.

TABLE NO. 5

SHATTER RESISTANCE OF MYLAR-GLASS LAMINATES

Mylar thick-ness (inches)	Adhesive	Press Cycle	Thermal Treat-ment	Shatter Temp.	High Vel-ocity Slug	Low Vel-ocity Slug	Remarks
.007	15% Epon 864 85% Epon 562 8.4 PHR* DMP-30	45 min. 140°C. 35 psi		-65°F.	x		Glass loss 1" dia. around point of exit. No delam-ination.
.007 (Fig. 11 right)	Same as above	Same as above	2 hrs. 400°F.	400°F.	x		Same as above. Some delamination around edges but retained glass.
.002 (Fig. 10 left)	Epon 652 8.4 PHR DMP-30	Same as above		-65°F.	x		Glass loss 5/8" around point of exit. Delamination along cracks but retained glass.
.002	Same as above	Same as above		Room temp.	x		Same glass loss. Good bond. No delamination.

* Parts per hundred parts of resin.

TABLE NO. 5 (Contd.)

SHATTER RESISTANCE OF MYLAR-GLASS LAMINATES

Mylar thickness (inches)	Adhesive	Press Cycle	Thermal Treatment	Shatter Temp.	High Velocity Slug	Low Velocity Slug	Remarks
.002 (Fig. 11 left)	Epon 652 8.4 PHR DMP-30	45 min. 140°C. 35 psi	2 hrs. 400°F.	400°F.	x		Delaminated. 50% glass loss.
.007 (Fig. 10 right)	Same as above	Same as above		-65°F.	x		7/8" to 1" glass loss around point of exit. Slight delamination along cracks. Retained glass.
.007	Same as above	Same as above		Room temp.	x		Glass loss 1/2" around point of exit. Slight delamination 2" around point of exit. Retained glass.
.011	Same as above	Same as above		-65°F.	x		1" - 1-1/4" glass loss around point of exit. Slight delamination along cracks. Retained glass.
.011	Epon 562 8.4 PHR DMP-30	45 min. 140°C. 35 psi		Room temp.	x		3/4" glass loss around point of exit. No delamination.
.011	Same as above	Same as above	2 hrs. 400°F.	400°F.	x		Delaminated. Mylar shrunk and cracked. Apparently locally overheated above 400°F

SHATTER RESISTANCE OF MYLAR-GLASS LAMINATES

Mylar thick- ness (inches)	Adhesive	Press Cycle	Thermal Treat- ment	Shatter Temp.	High Vel- ocity Slug	Low Vel- ocity Slug	Remarks
.007	15% Epon 864 85% Epon 562 8.4 PHR DMP-20	45 min. 140°C. 100 psi	2 hrs. 400°F.	400°F.		x	Shattered into large pieces. Some delamination.
.007 (Fig. 12 right)	Same as above	Same as above	None	Room temp.		x	Little delami- nation. Laminate remained intact.
.007	Same as above	Same as above	2 hrs. 400°F.			x	Glass treated with vinyltrichlorosi- lane. Delamina- tion and loss of large pieces of glass around point of impact.
.007 (Fig. 12, left)	Same as above	Same as above	Same as above	400°F.		x	Mylar VTS treat- ed. Sheared lam- inate with very little delamination.

As the above data indicate, Epon resins cured with DMP-30 tend to become brittle at elevated temperatures.

3. Stability to Accelerated Weathering Tests

Three samples of 4" x 6" laminates made with .007" Mylar were subjected to 136 hours in the Weatherometer. Epon 562, cured with 8.4 parts of DMP-30 triacetate per hundred parts of resin, was used as the adhesive. The Weatherometer cycle was 15 minutes exposure to the light of a carbon arc, followed by 3 minutes of water spray to simulate rain.

Results of these tests are shown below:

Sample	Results
1. No surface treatment	15% delaminated
2. Mylar-vinyltri-chlorosilane treated	40% delaminated
3. Glass-vinyltri-chlorosilane treated	30% delaminated

The delamination in all cases started in one corner and pro-
ceeded toward the center of the laminate and was apparently due to the
response of the adhesive to the water spray. There was no evidence of
delamination due to thermal shock. No optical defects were introduced
by the exposure to the light of the carbon arc. In subsequent tests it is
suggested that the laminates be edge sealed to prevent delamination from
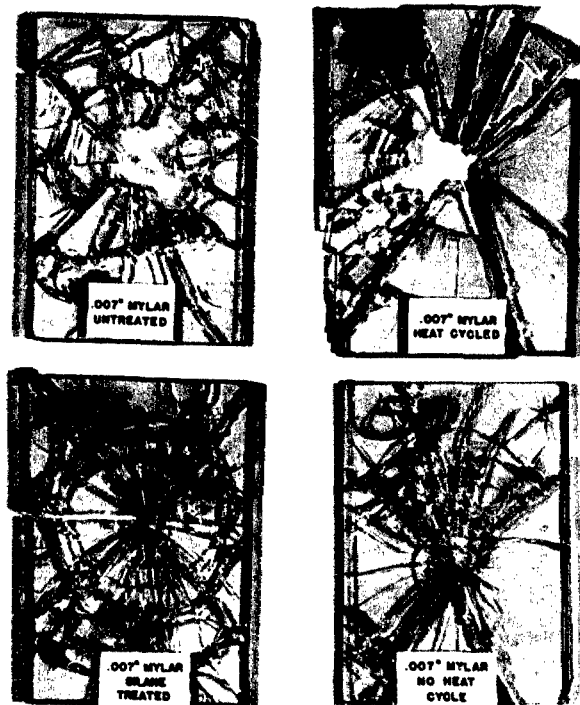contact of the adhesive layer with the water spray.
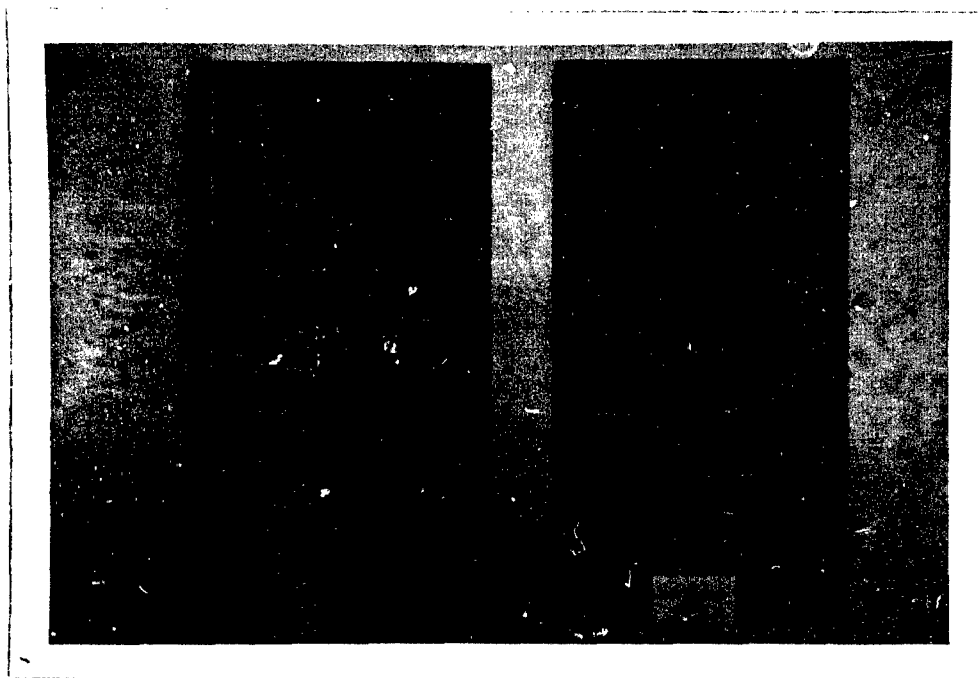
Figure 10. Low Temperature Shatter
Resistance of Mylar-Glass Laminates
to a High Velocity Projectile.

Figure 11. High Temperature Shatter
Resistance of Mylar-Glass Laminates
to a High Velocity Projectile.

Figure 12. Comparison of Shatter Resistance
of Mylar-Glass Laminates. The two laminates
at the left were shattered at 400°F. The lami-
nate at the upper right was exposed to 400°F.
for 2 hours and shows the tendency of the adhe-
sive to become brittle after thermal treatment.

APPENDIX I

TRADE NAMES AND SUPPLIERS

BUTACITE   -   E. I. duPont de Nemours & Company

MYLAR   -   E. I. duPont de Nemours & Company

NYLON   -   E. I. duPont de Nemours & Company

UFORMITE MX 61   -   Rohm & Haas Co.

FLEXOL 3GH   -   Carbide & Carbon Chemical Corp.

SILASTIC   -   Dow-Corning Corp.

SILON   -   Minnesota Mining & Mfg. Co.

KEL F   -   M. W. Kellogg Company

TRITHENE   -   Visking Corp.

ARALDITE   -   Ciba, Inc.

EPON   -   Shell Development Co.

DMP-30   -   Shell Development Co.

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